Thermal analysis in eco-concrete research

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Introduction

Concrete production: 10 billion ton concrete each year, 3 billion ton cement

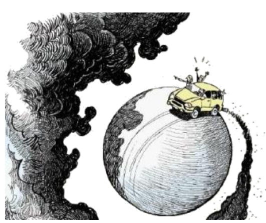
Consumption of natural raw materials

» **42%** of produced aggregates is for concrete production

» **1 kg** cement = **1.6 kg** raw materials

Production of waste

» **850 million tons** construction and demolition waste whereof **40-67%** is concrete



Emission of CO_2

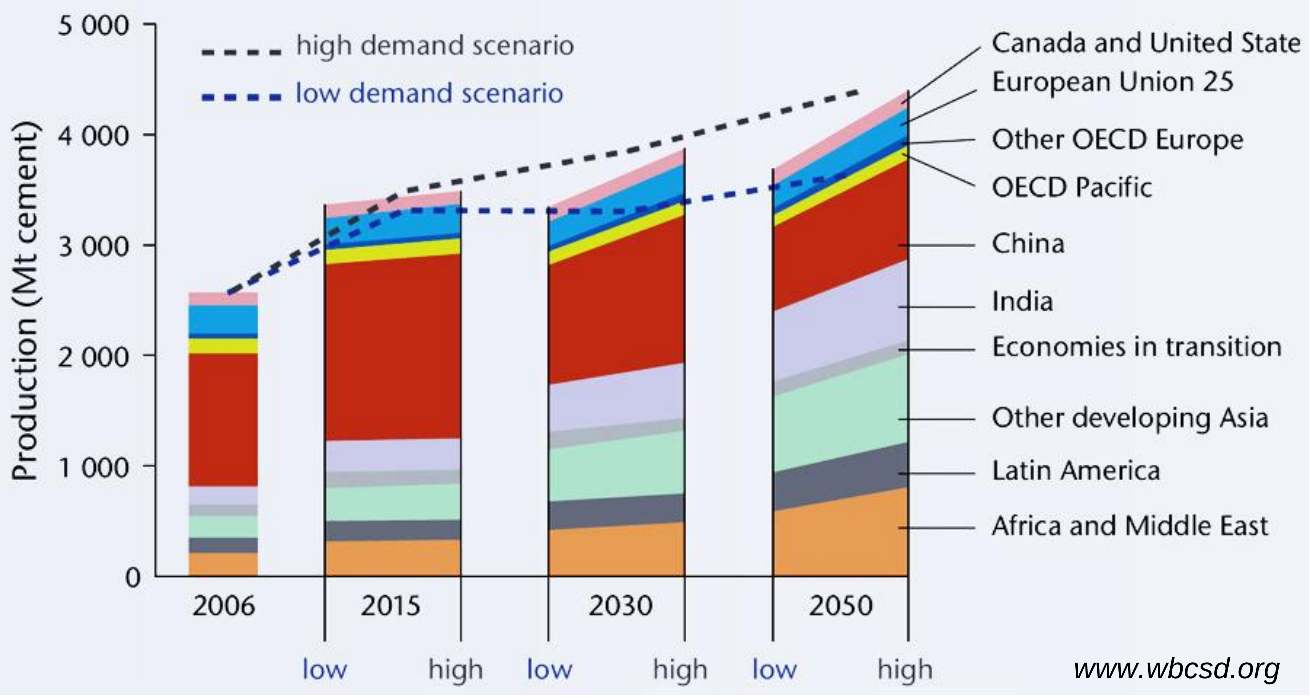
» **1.6 billion tons** each year which is around **5-8%** of the total CO_2 emissions

~ 40% energy required for cement production (at > 1400 °C)

~ 60% calcination of limestone (to produce cement)

$$CaCO_3 \rightarrow CaO + CO_2$$

Evolution



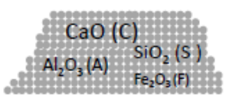
www.wbcsd.org

What is concrete
Overview
Portland Clinker

Cement hydrates
= creation of adhesive bonds

CSH gel, ettringite, portlandite

CO_2



Raw meal

Clinker production

heating

1450°C

Clinker

Cement production

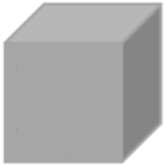
milling clinker with $CaSO_4$

Cement

H_2O

hydration

Fine and coarse granulates >60 %



Concrete

Formation of alite,
belite, aluminate, ferrite

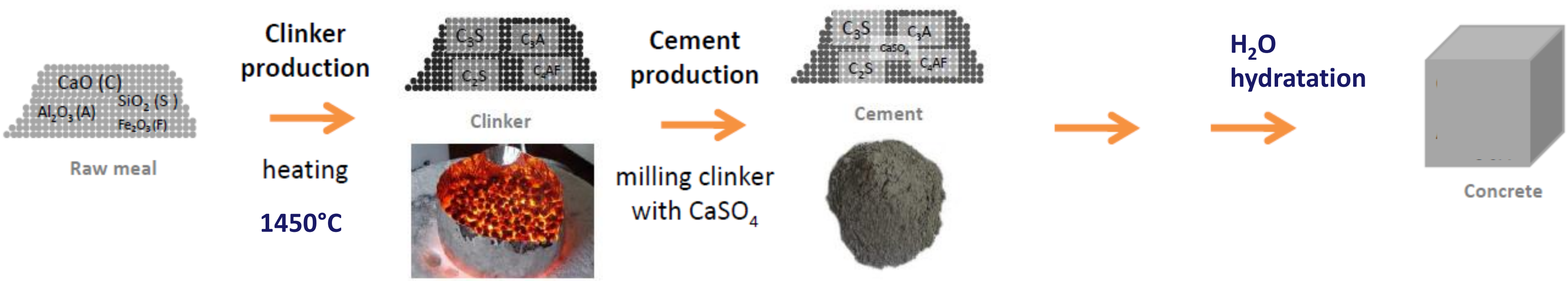
Ca-source
Si-source
Al-source
Fe-source

What can be done ?

Portland Clinker / alternative binders

<u>Clincker production using</u> industrial byproducts and waste.
slag, <u>fly ash,</u> silica (glass powder)

<u>Replacement</u> of clinker and cement by industrial byproducts and waste : supplementary cementitious materials (SCMs)
<u>fly ash</u>, <u>slag,</u> silica (glass powder)



Use of the best technology
Thermal efficiency of kiln and cooler systems

Use of demolition waste as aggregate

Use of alternative fuels (i.e. solvent waste)

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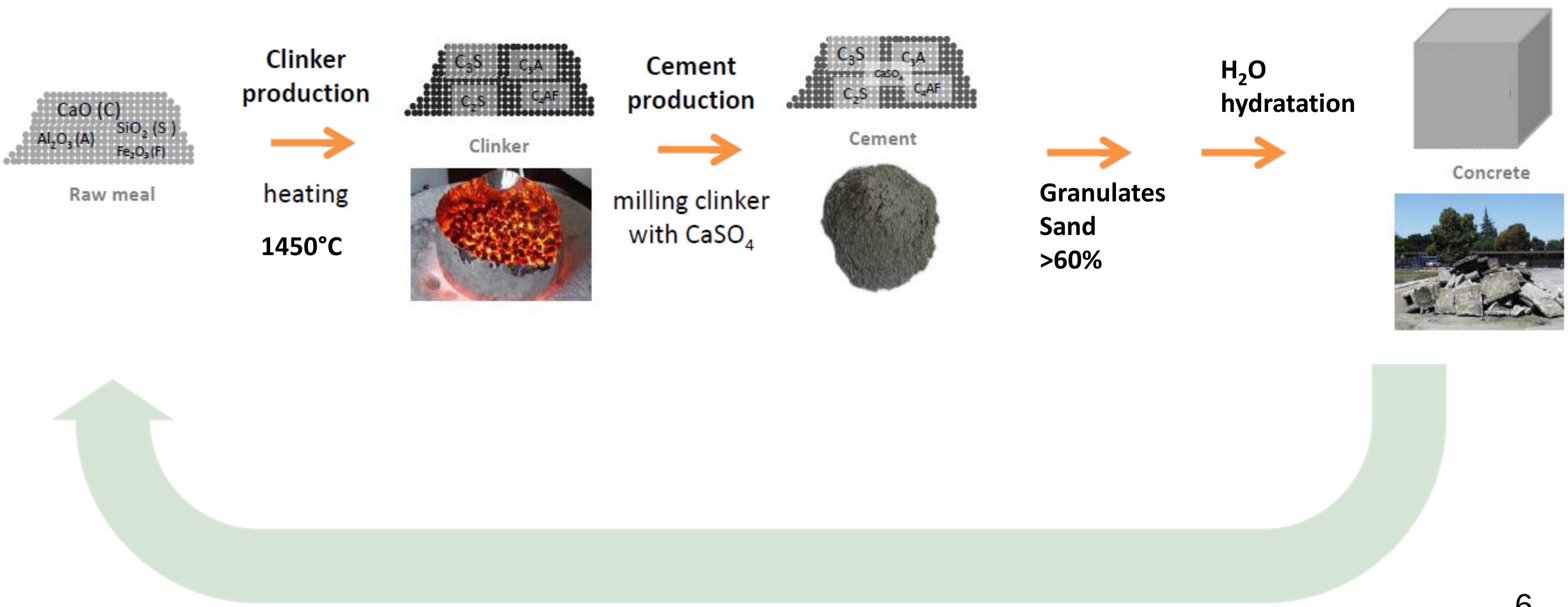
What can be done ?



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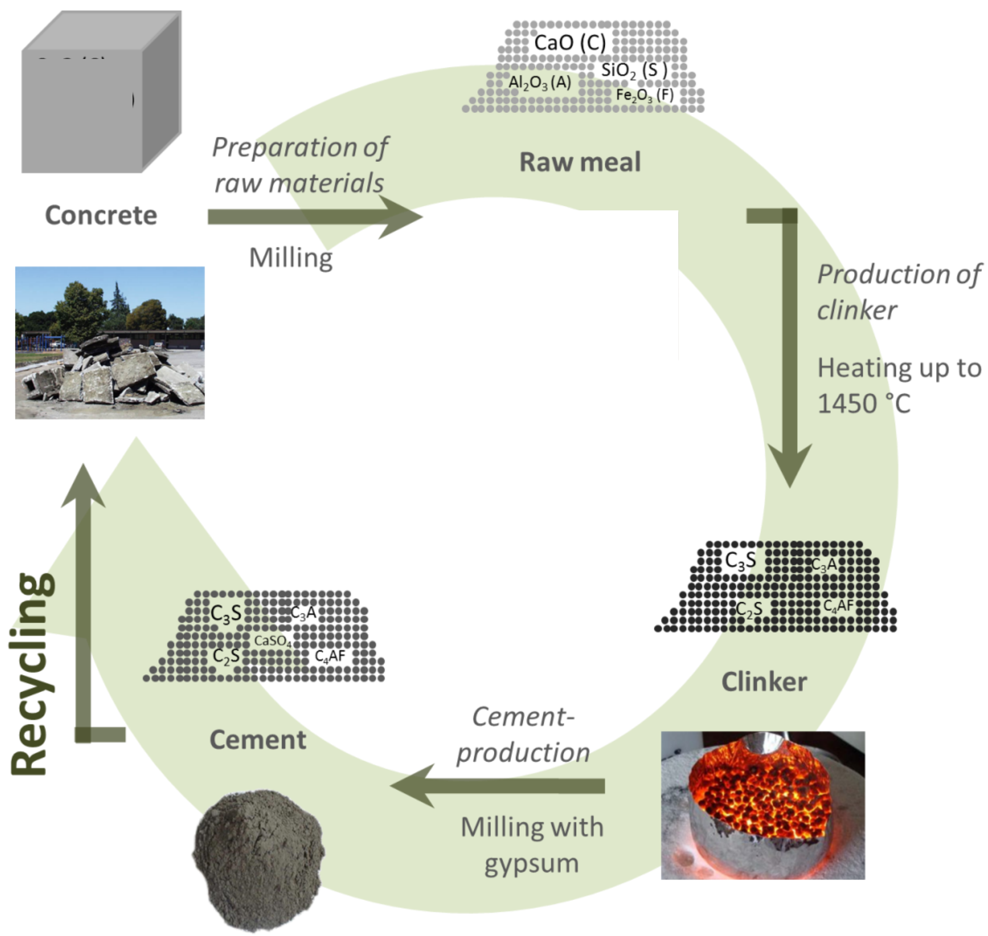
What can be done ?

Complete recyclable concrete

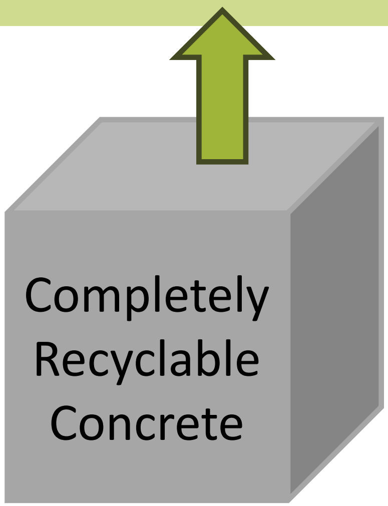
Cradle to cradle Concept

M. De Schepper



Design of a concrete which could be used for making a new clincker

Necessary condition:
Chemical composition CRC
=
Chemical composition
cement raw meal



Most important ratios:

LSF: lime saturation factor	Ca versus (Si, Al, Fe)
SM: silica modus	Si versus Al, Fe
AM: alumina modus	Al versus Fe

To make a good clincker:
composition should lie between certain limits

1. Cement paste: hydrated + crushed
   CEMI 52.5N

2. CRC: hydrated + crushed

   CEMI 52.5N
   +
   Components:
   Limestone aggregates (Gaurain, Soignies)
   Limestone filler
   Diorite (Lessines)
   Fly ash
   Copper slag

Two raw materials:

a CRC and a CEMENT PASTE (CP)

	CRC	**CP**
CaO	64.99	62.04
SiO_2	20.97	18.99
Al_2O_3	6.10	5.97
Fe_2O_3	2.50	4.23
MgO	2.53	0.96
SO_3	1.02	3.18
K_2O	-	0.66
Na_2O	-	0.46
LSF	0.96	0.98
SM	2.44	1.86
AM	2.44	1.41

Good for clincker production

Cement paste

Clinker production

heating

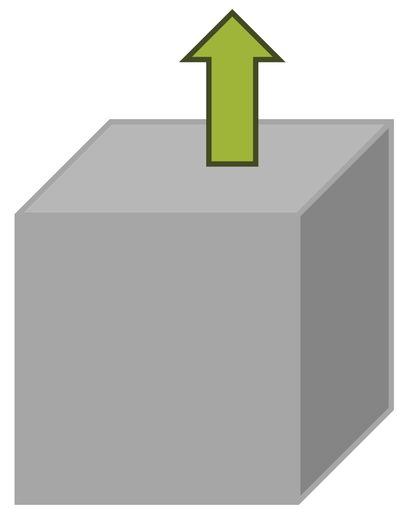
Clinker

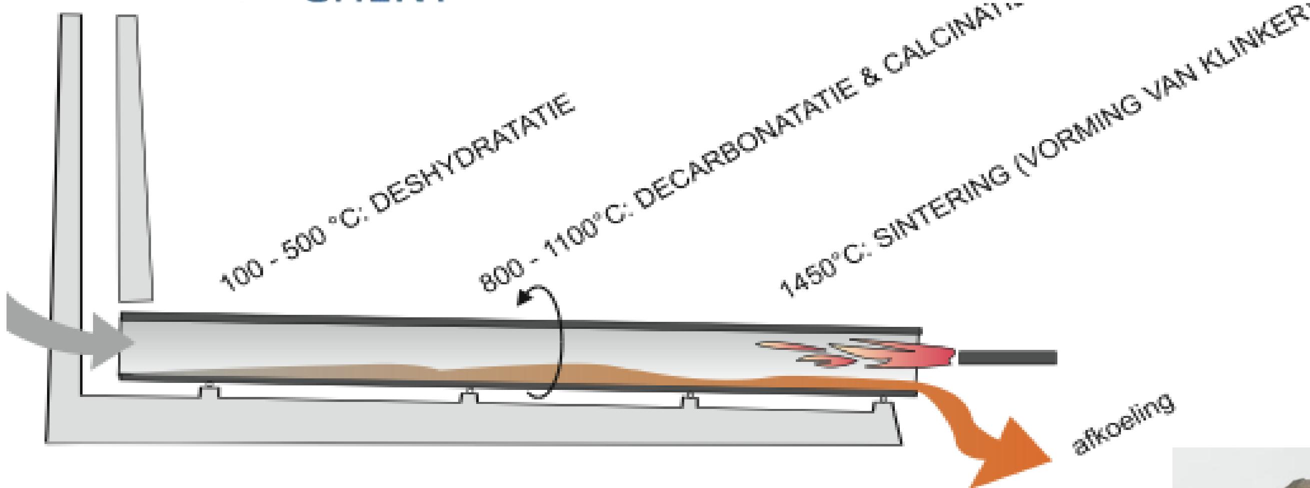
CRC

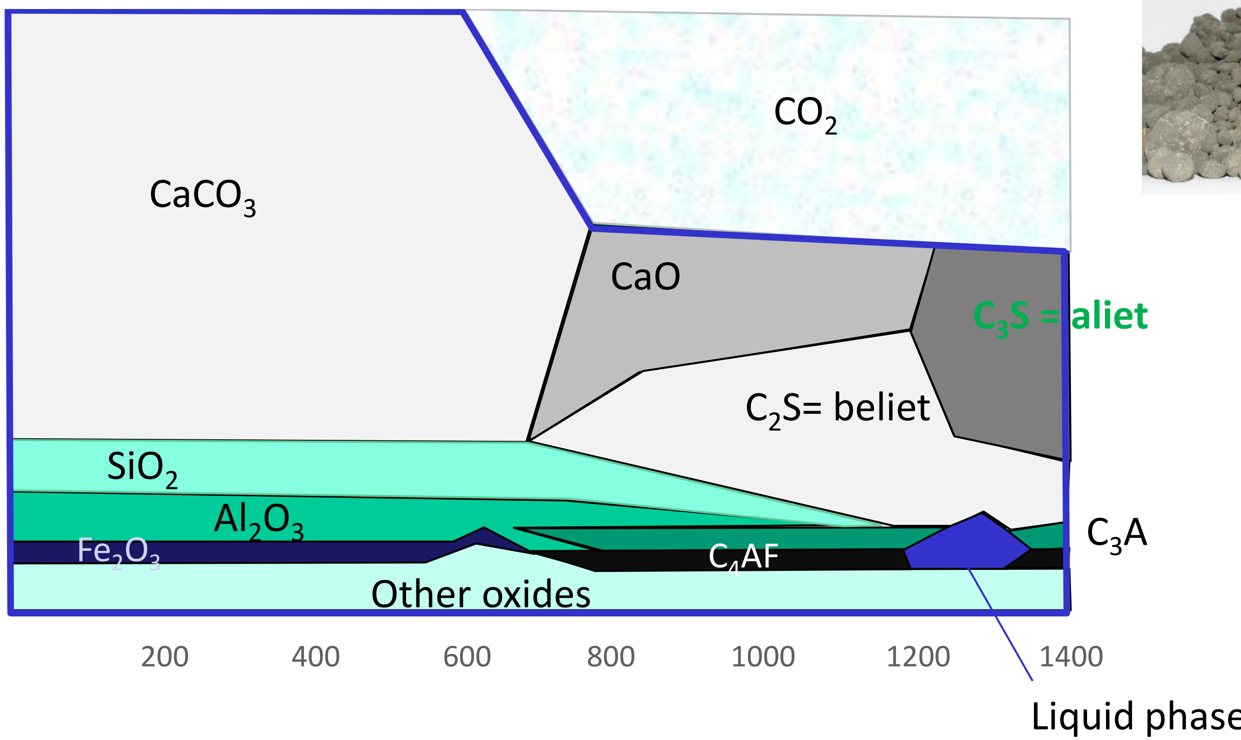
1450°C

Formation of alite, belite, aluminate, ferrite

Question:
How does this mixture behave during reclinkering?




100 - 500 °C: DESHYDRATATIE
800 - 1100°C: DECARBONATATIE & CALCINAT
1450°C: SINTERING (VORMING VAN KLINKER)
afkoeling

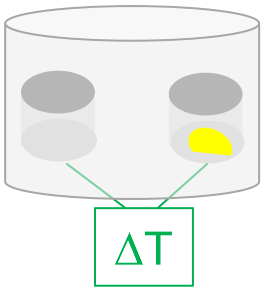

$CaCO_3$
CO_2
CaO
C_3S = aliet
C_2S= beliet
SiO_2
Al_2O_3
Fe_2O_3
C_4AF
C_3A
Other oxides
200
400
600
800
1000
1200
1400
Liquid phase

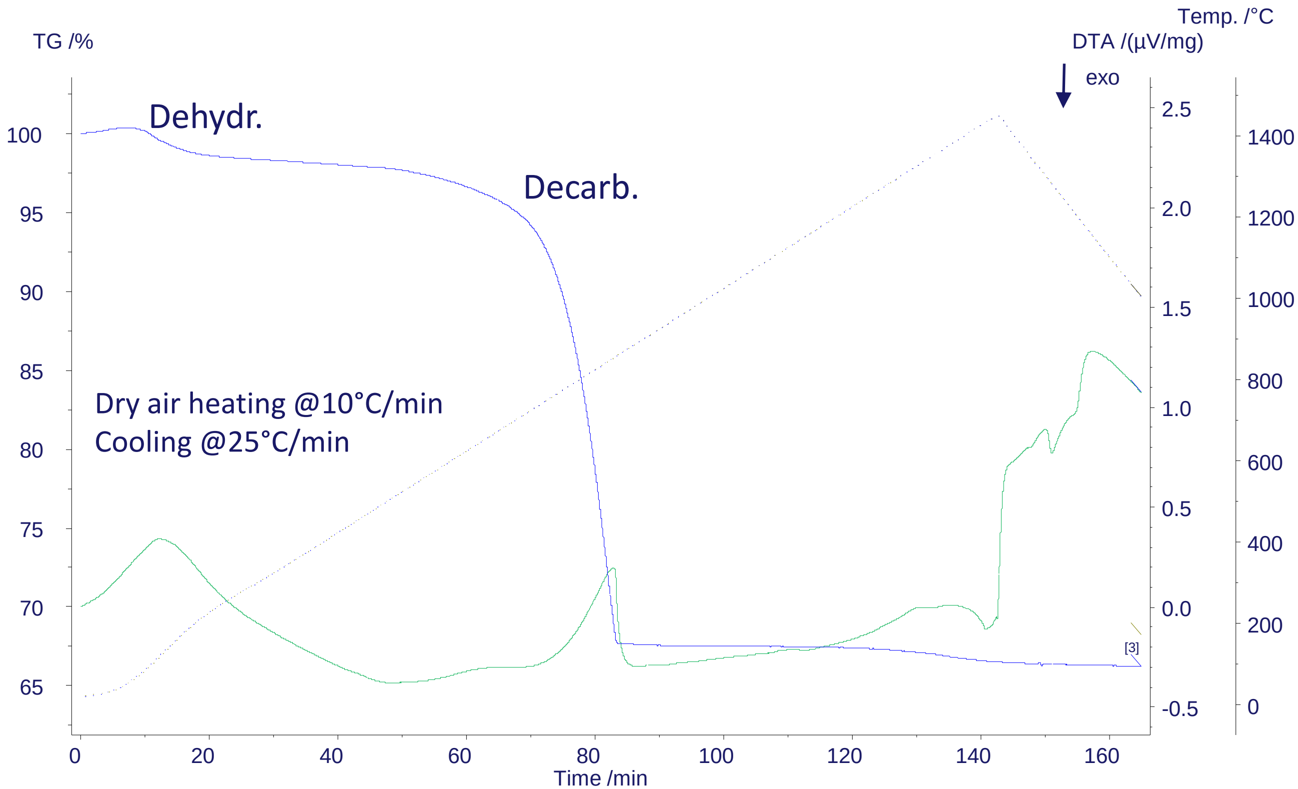
Clinckering Reactions, Ruben Snellings

1. Thermogravimetry /Differential thermal analysis

2. XRD-HTXRD

Clinckering Reactions
TGA-DTA,
heating and fast cooling of a CRC





Base line is not flat

- Geometry of <u>furnace</u>
  Heat transfer towards cup
  Compare with blanc

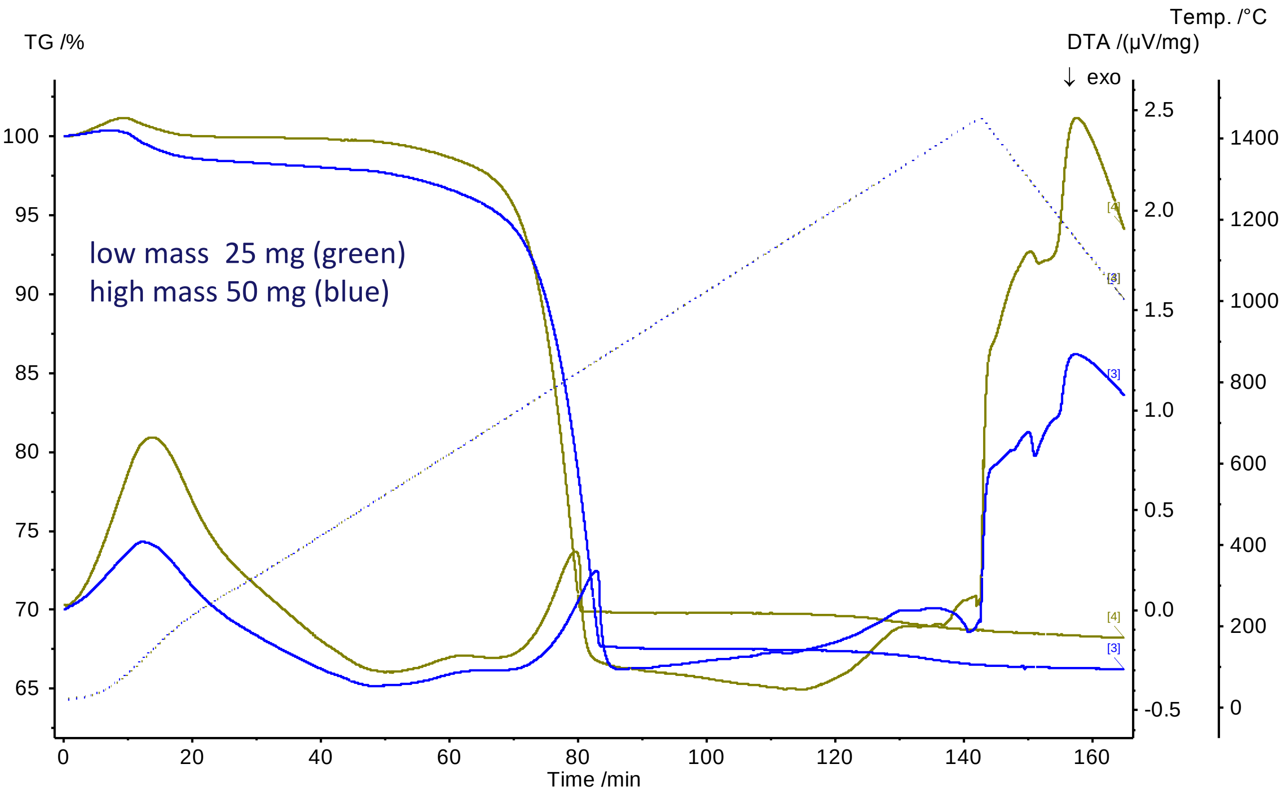
- There is a <u>sample</u>
  * emissivity
  * Thermal conduction

Clinckering Reactions

TGA-DTA, mass-difference baseline method

Yang & Roy, Thermochimica acta, 1999

DTA curve derived from a small mass sample as the baseline for a large mass sample using the same material.



diminishes

- ``apparatus effect''

asymmetric heat transfer problem attributed to the and

-``sample influence''

improving the linearity between the DTA curve and enthalpy change.

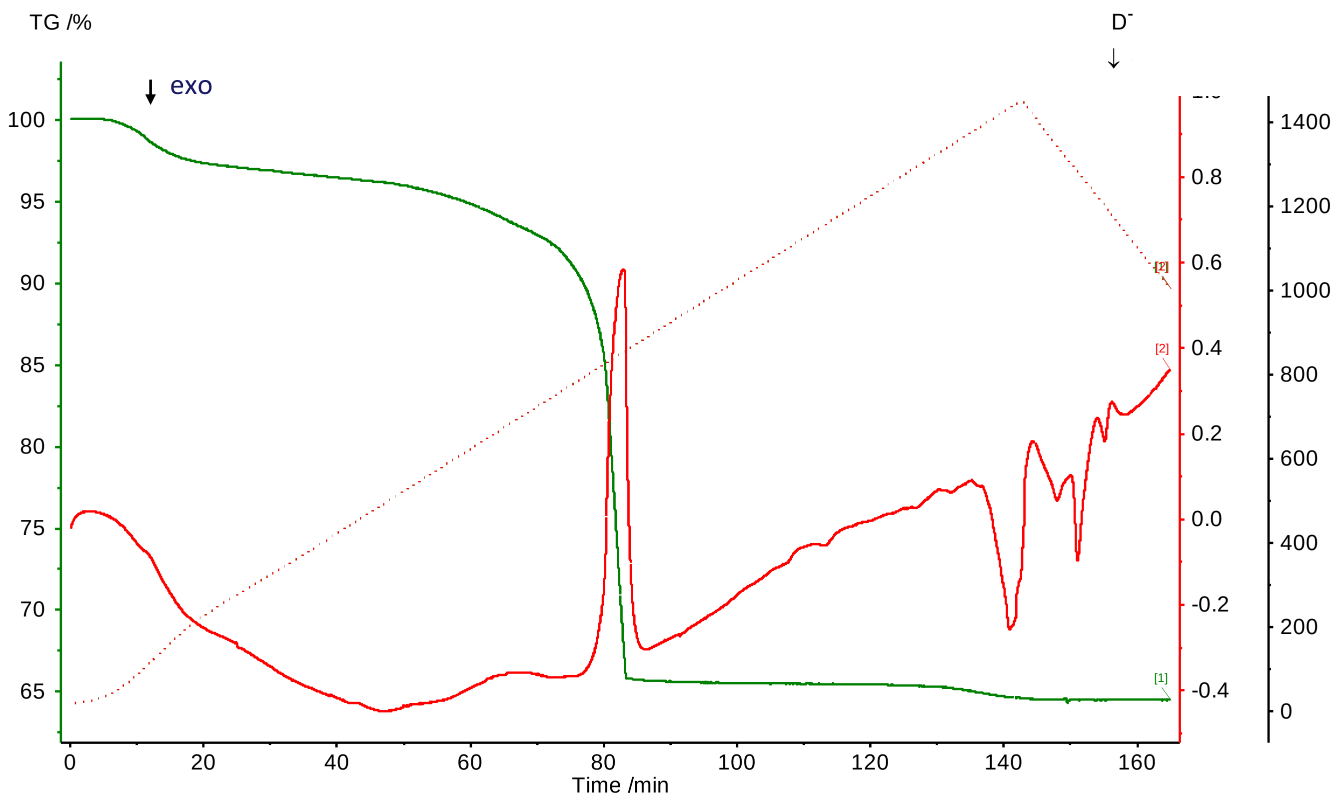
Clinckering Reactions

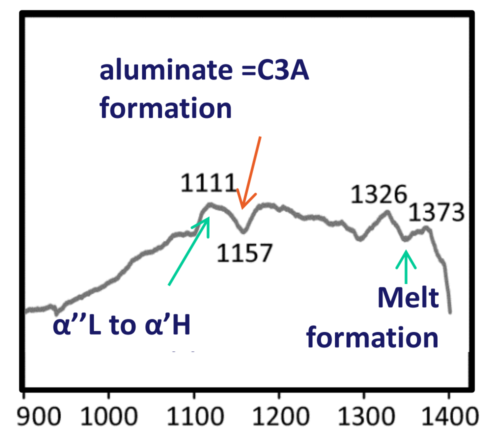
TGA-DTA,

heating and fast cooling of a CRC

Higher temp: possible explanations: melt formation and crystallisation, polymorphic transformations of alite and belite

Much better resolution on endothermal and exothermal events





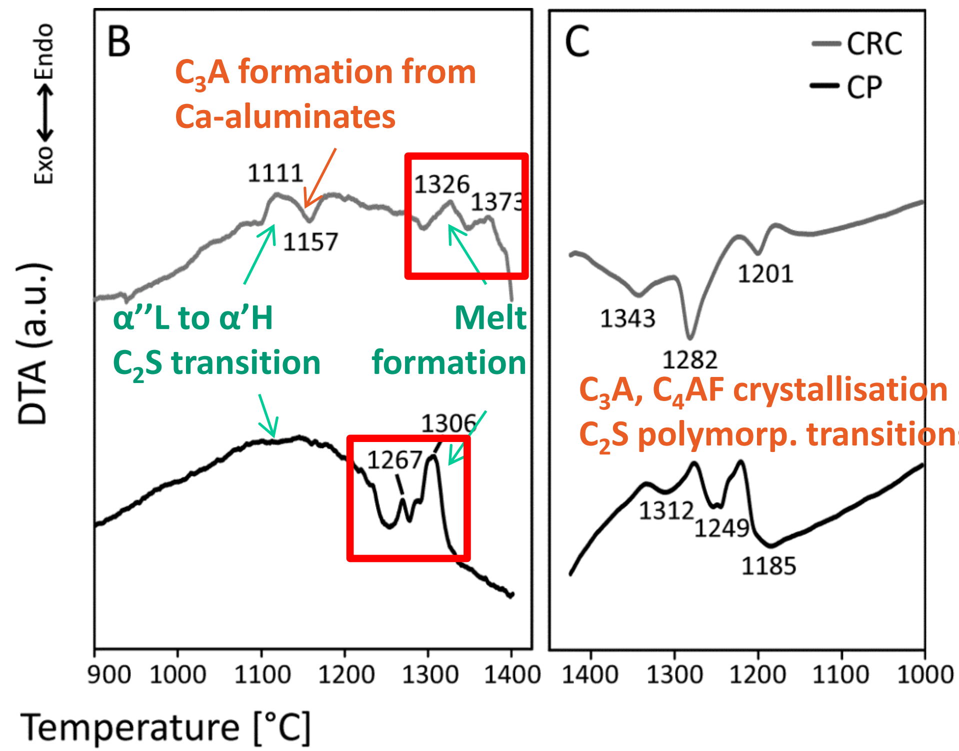
Clinckering Reactions

TGA-DTA

DTA curves for CRC and Cement Paste (CP) during heating (B) and cooling (C)

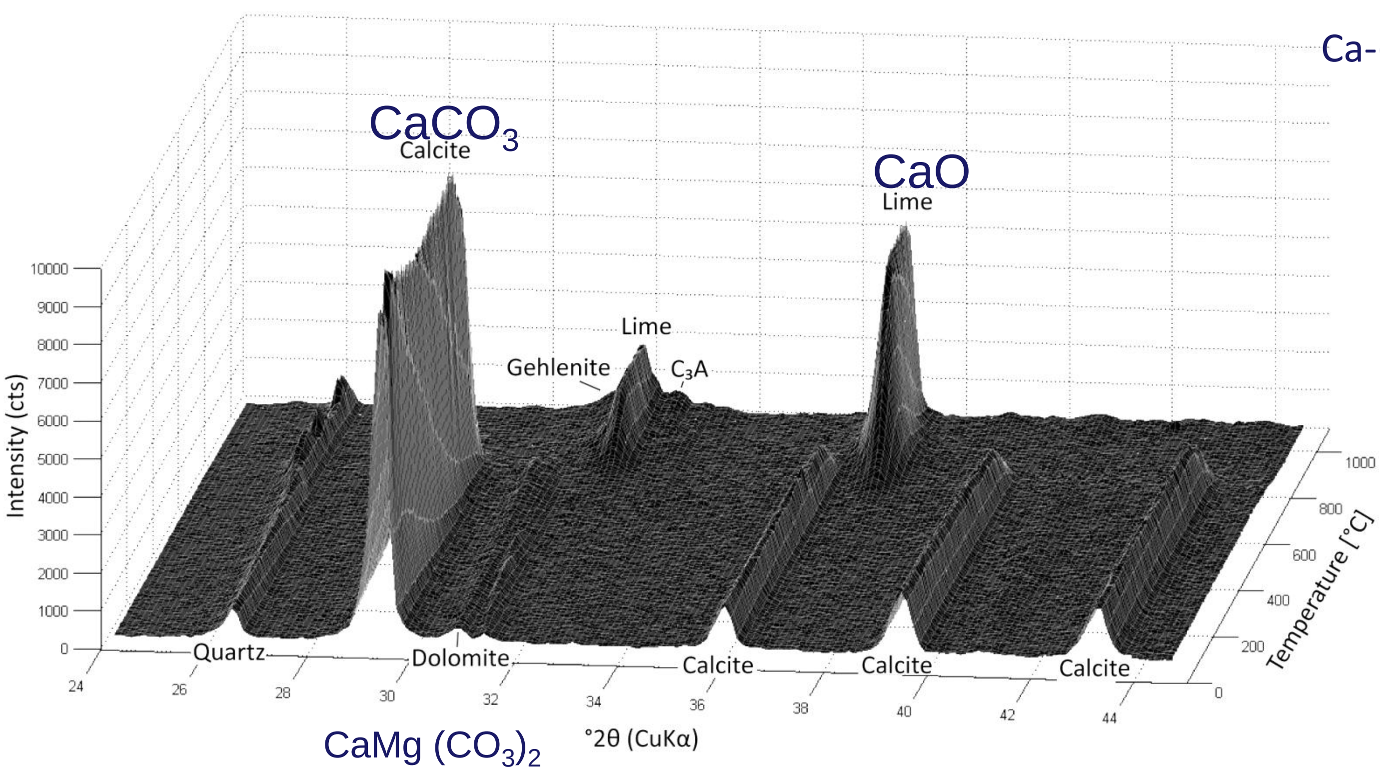
Lower T of melt formation and cooling exotherms

Indicative for
better burnability of CP



Clinckering Reactions
HTXRD

In situ XRD measurements
25 – 1050 °C:
- Calcite & dolomite decomposition
- Decomposition of quartz
- Formation of intermediate phases



Ca-(alumino-)silicates

- Gehlenite (C2AS)
- Yeelimite (C4A3S)
- Belite (C_2S)
- Mayenite (C12A7)
- Lime :CaO
- Aluminate: celiet (C3A)
- Ferrite (C4AF)

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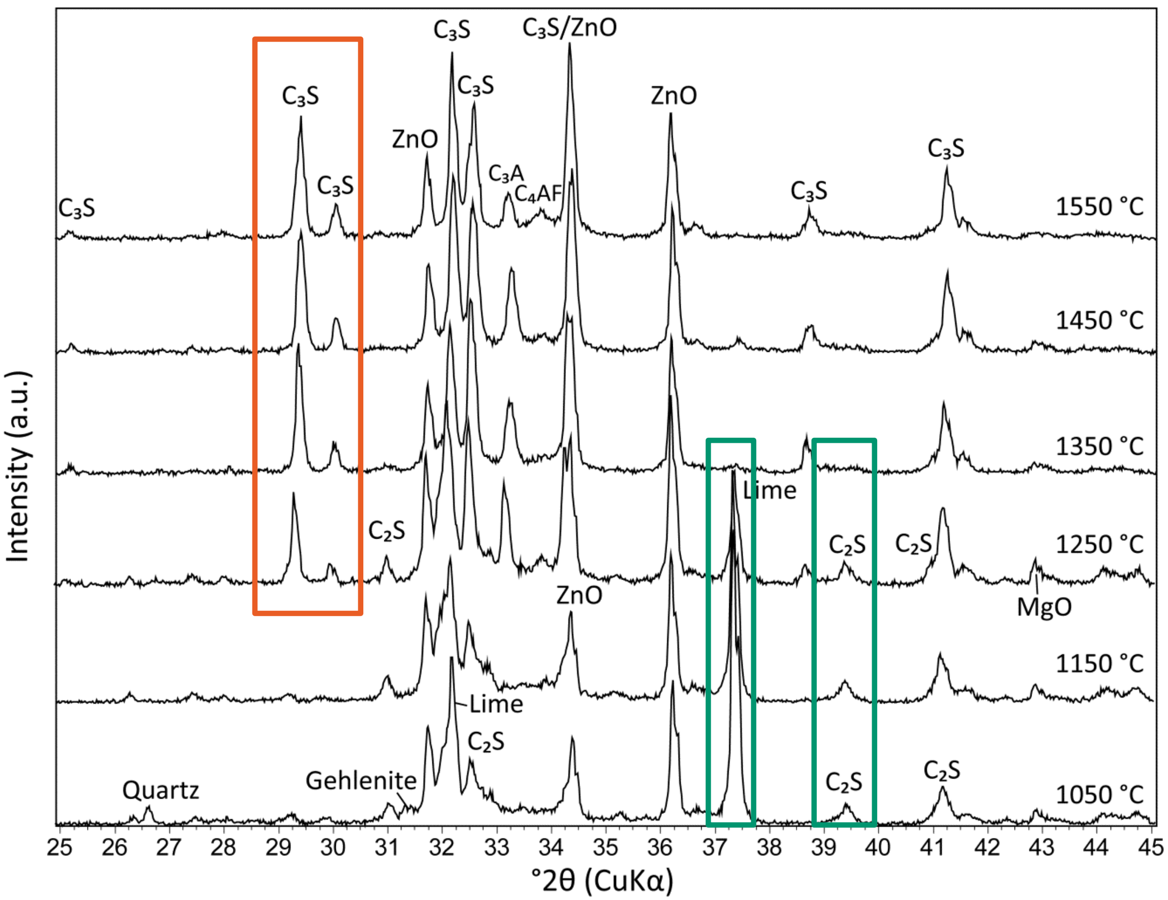
Clinckering Reactions

XRD, after calcination



Ex situ XRD measurements,
1050 – 1550 °C, dwell 1h

- C2S + CaO → C3S
- Decomposition of intermediate phases to form main clinker phases

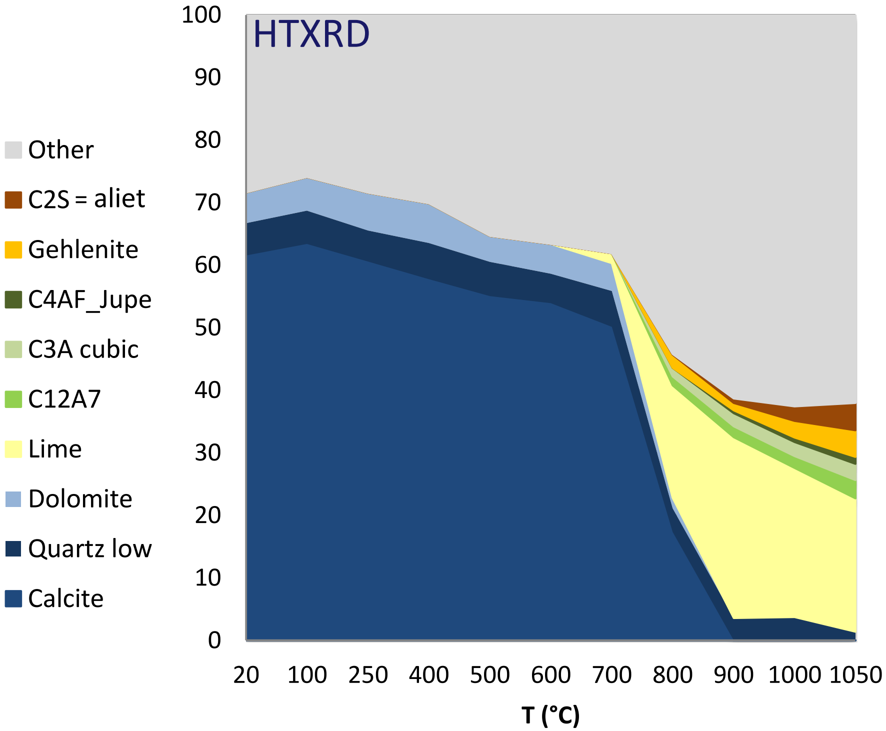
End product

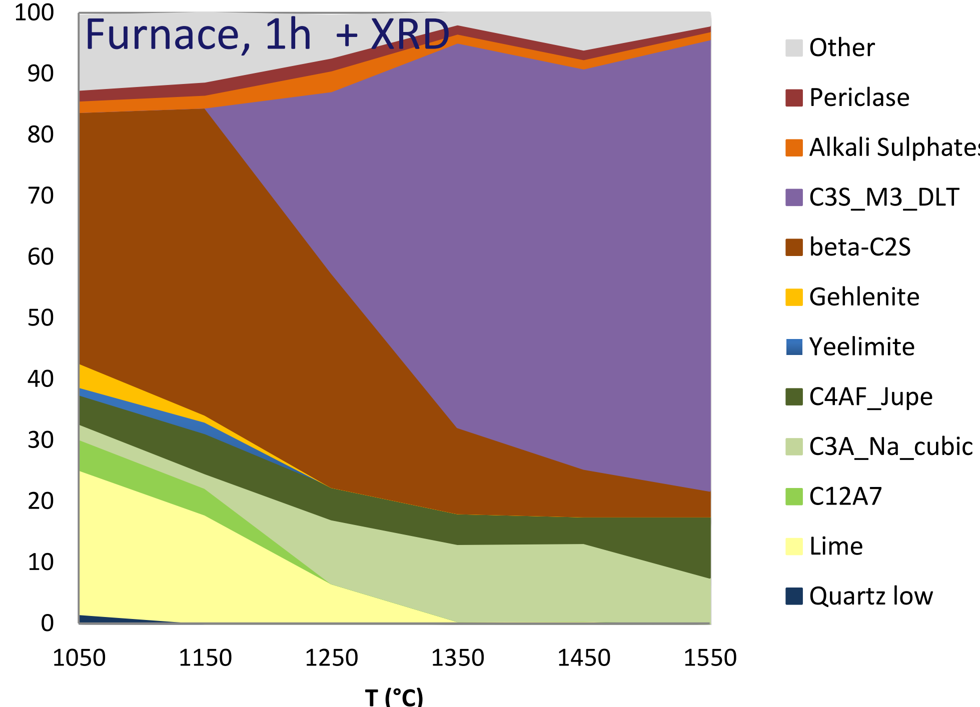
- Alite (C3S = Ca_3SiO_5)
- Belite (C2S = $Ca_2\,SiO_4$)
- Aluminate (C3A = $Ca_3Al_2O_6$)
- Ferrite (C4AF= $Ca_2\,(Al,Fe)_2O_5$)

ZnO intern standard for Rietveld analysis

Clinckering Reactions

Rietveld





Rietveld analysis gives a quantitative view on the occurring reactions:
Using : internal standard
Using data from TGA: mass loss ,melt formation

1050 – 1150 °C:

- Extensive crystallisation of C_2S
- C_2AS, $C_4A\check{S}$ (yeelimite), $C_{12}A_7$, C
- Quartz decomposition

1250 – 1450 °C

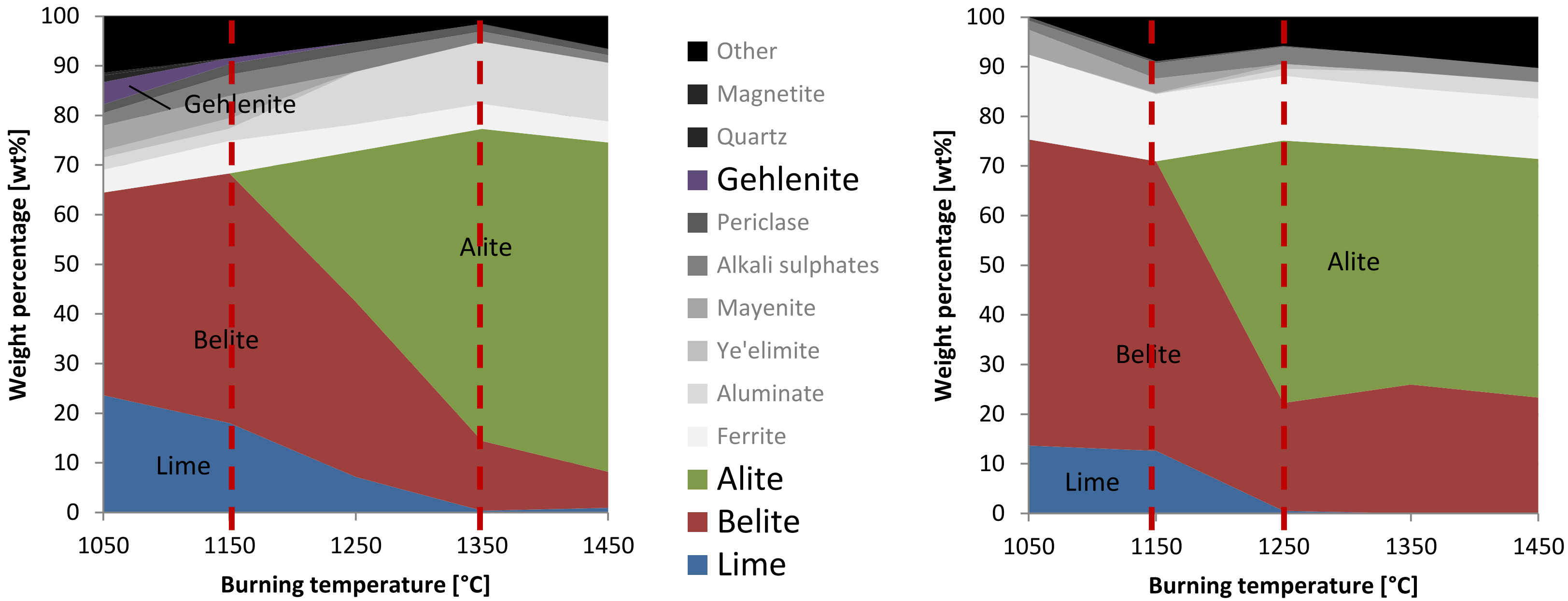
- Intermediate Ca-aluminates form C_3A
- $C_2S + C \rightarrow C_3S$ (gradual increase)

1450 -1550 °C

- C_4AF and C_3S are formed at the expense of C_3A

Clinckering Reactions

CRC versus Cement paste



CRC **Cement Paste**

Comparison with CRC:

- in cement:
  - Lower aliet / beliet due to solid solution in C_2S
  - Higher C_4AF = ferrite (higher Fe_2O_3 content)

Why?: more S => more / melt at low temperature. : faster

S in Belit: less alite

Clinckering Reactions

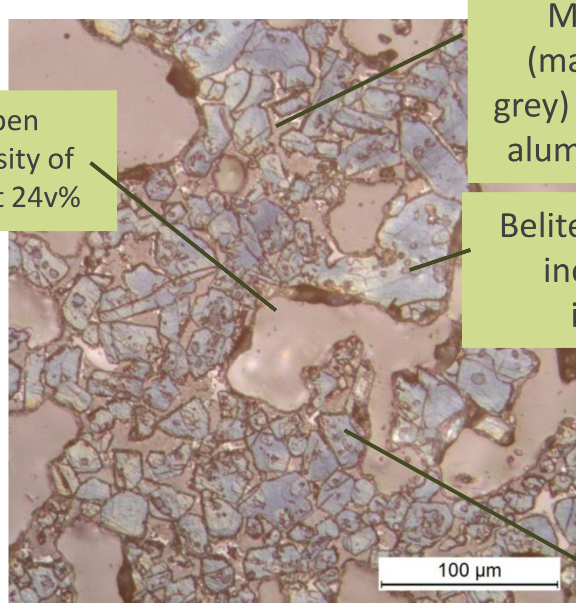
Microscopy, **Traditional clinker phases are formed!**

CRC versus cement paste, burned at 1450°C

Open porosity of about 24v%

Melt (mainly grey) rich in aluminate

Belite mainly as inclusions in alite



CRC

At 1450°C more open pores

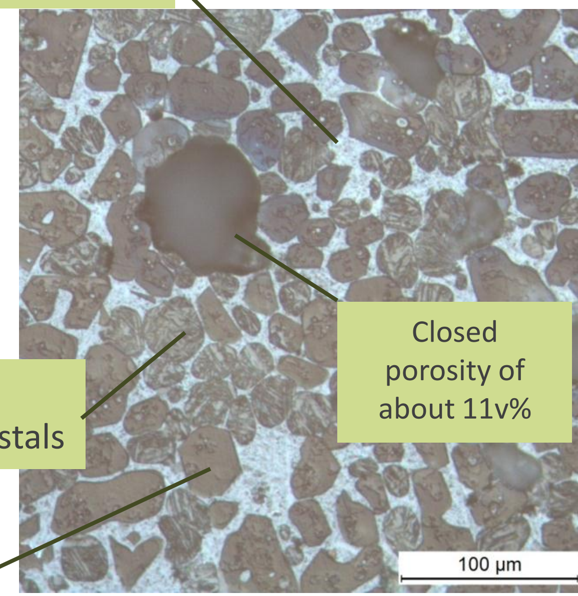
More alite

Alite

Belite as individual crystals

Melt (mainly bright/white) rich in ferrite

Closed porosity of about 11v%



Cement Paste

- more and earlier melt formation
- earlier formation of well-formed alite/belite crystals
- better distribution of the crystals in the melt
- lower porosity

⇨ **cement paste clinker has a better burnability**

General conclusions

In the cement paste clinker

- more and earlier melt formation
- earlier formation of well-formed alite/belite crystals
- better distribution of the crystals in the melt
- lower porosity

⇨ **cement paste clinker has a better burnability**

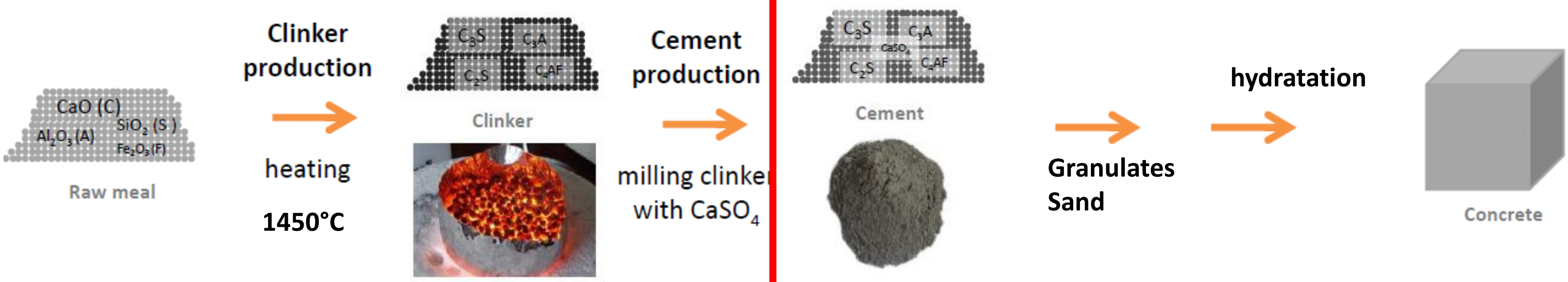
This effect is probably caused by its higher sulfur content

S: acts as flux

-Lowering melitng temp. (seen in TGA)
-Reduces melt viscosity
-Stabilizes belite => less alite

	CRC	CP
CaO	64.99	62.04
SiO_2	20.97	18.99
Al_2O_3	6.10	5.97
Fe_2O_3	2.50	4.23
MgO	2.53	0.96
SO_3	1.02	3.18

Next step : hydration



Formation of alite, belite, aluminate, ferrite

Cement hydrates
= creation of adhesive bonds

Question:
How does the cement behave during hydration?

Clinker production

CRC → **clincker** → **cement**

heating

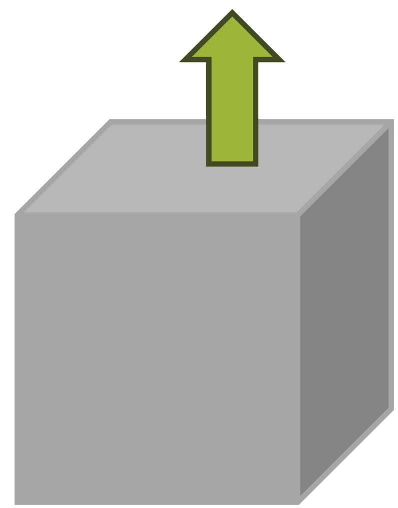
1450°C

+ $CaSO_4$

+ 40% H_2O hydratation

Commercial Cement →
CEM I 52.5 N

+ 40% H_2O hydration



Cement hydration

Alite + water:
$2Ca_3OSiO_4 + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$ (= **fast**) *-121.1 KJ/mol*

Belite + water:
$2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2$ (= **slow**) *-45.1 KJ/mol*

Aluminate + water + gypsum: *-263.0 KJ/mol*
$Ca_3(AlO_3)_2 + 3CaSO_4 + 32H_2O \rightarrow Ca_6(AlO_3)_2(SO_4)_3.32H_2O$

Ferrite +water + gypsum:
$2Ca_2AlFeO_5 + CaSO_4 + 16H_2O \rightarrow Ca_4(AlO_3)_2(SO_4).12H_2O + Ca(OH)_2 + 2Fe(OH)_3$

Reaction rate: formation $Ca(OH)_2$
bound H_2O
heat of hydration

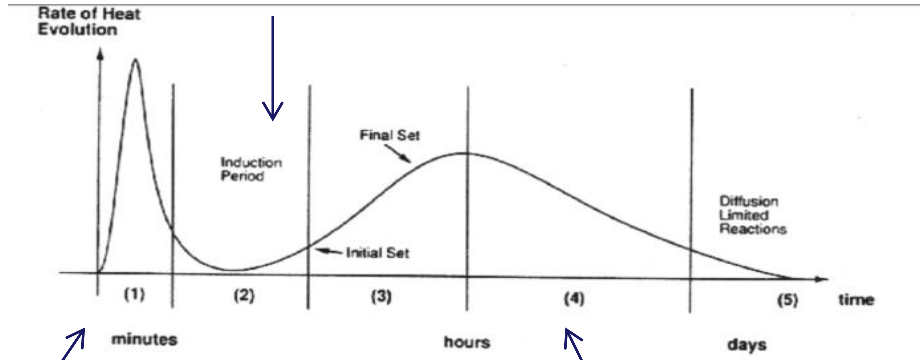
Isothermal calorimetry

Early stage of hydration

Apparatus: TAM air, TA instruments :

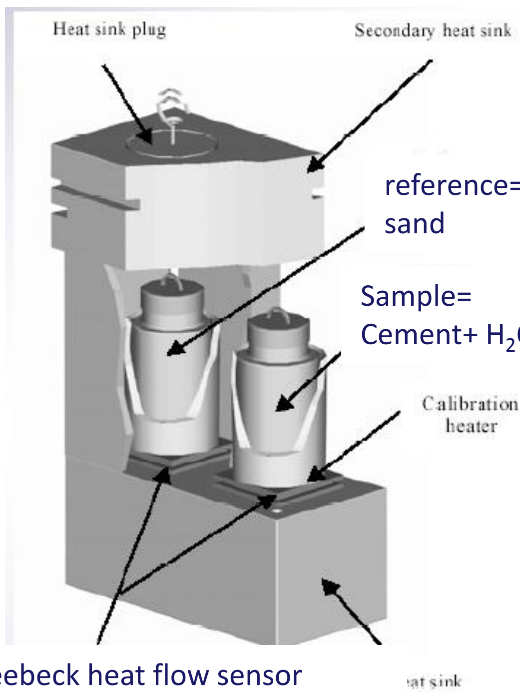
2 ampules, temp constant

Dormant period



1° period
Ca^{2+}
OH^-

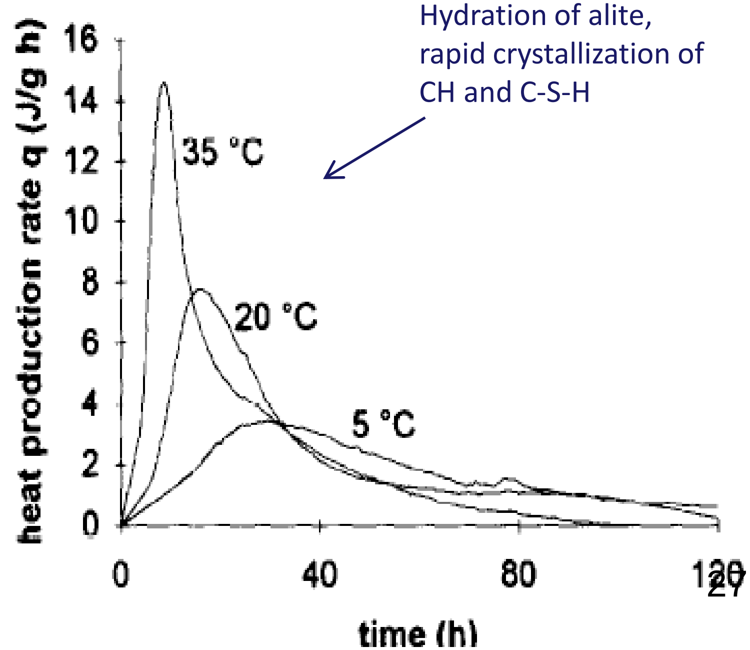
Hydration of alite, rapid crystallization of CH and C-S-H



reference= sand

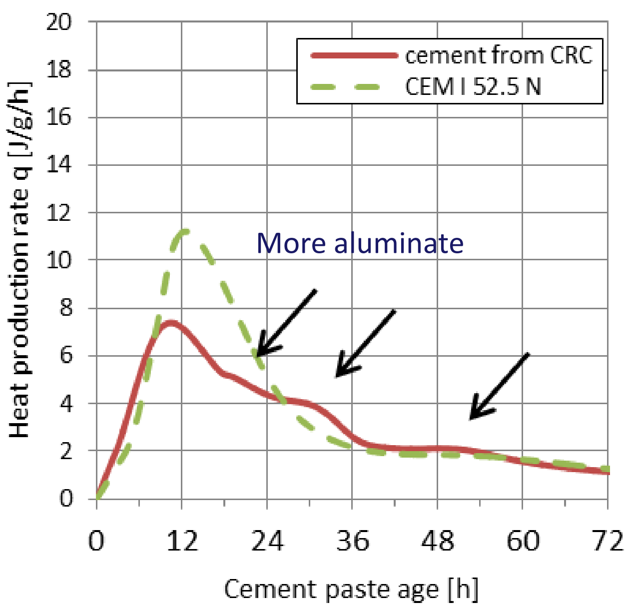
Sample= Cement+ H_2O

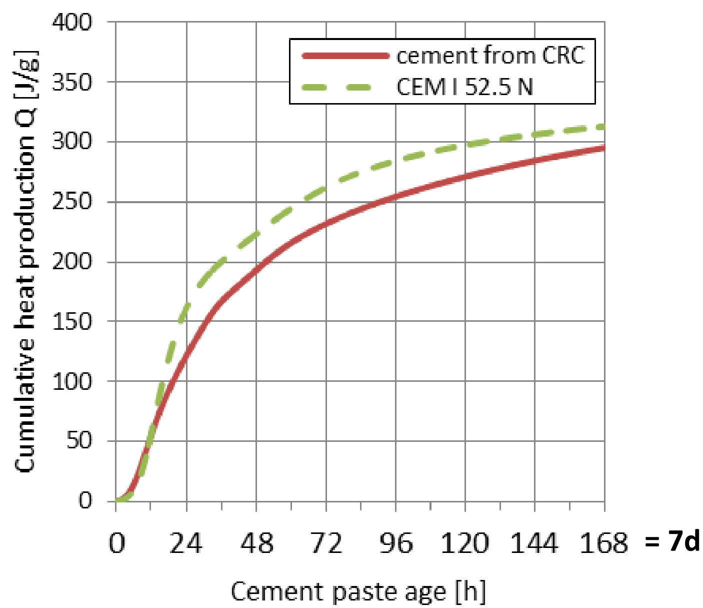
Seebeck heat flow sensor



Isothermal calorimetry

- Shows us the reaction speed in the first couple of hours, days….





Hydration of regenerated cement is **slower, but after 7 days** the cumulative hydration heat is **approaching the one of CEM I 52.5 N**

Size of grains is of major importance..

TGA, DTA

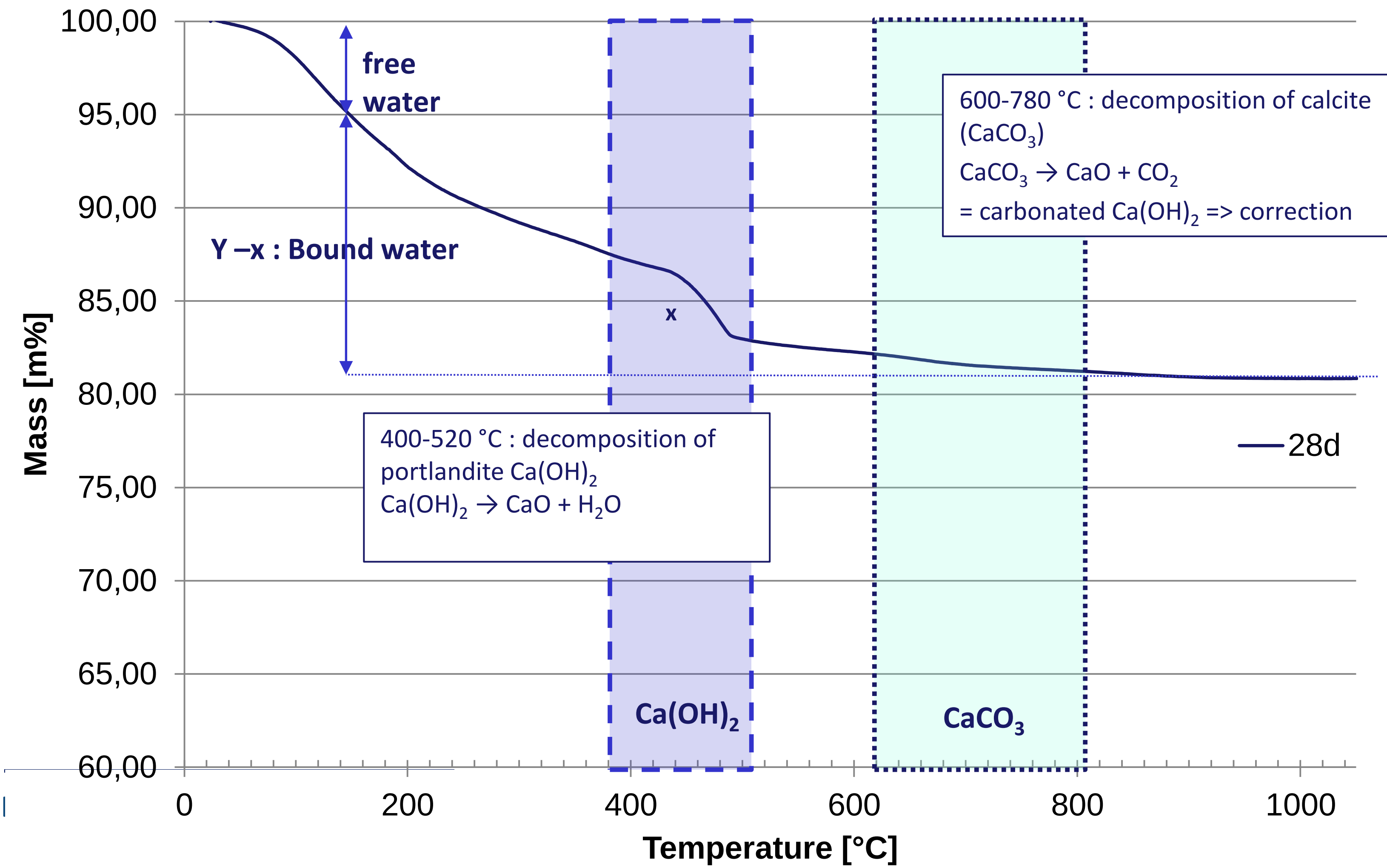
Cement + H2O -> react for 1h, 3 h , 6h, 9h, 1d, 2d, 3d, 7d, 28 d

and stop the reaction by
- Freeze drying
- Solvent Exchange: soaking in dry solvent to replace capillary water ethanol / isopropanol + drying.

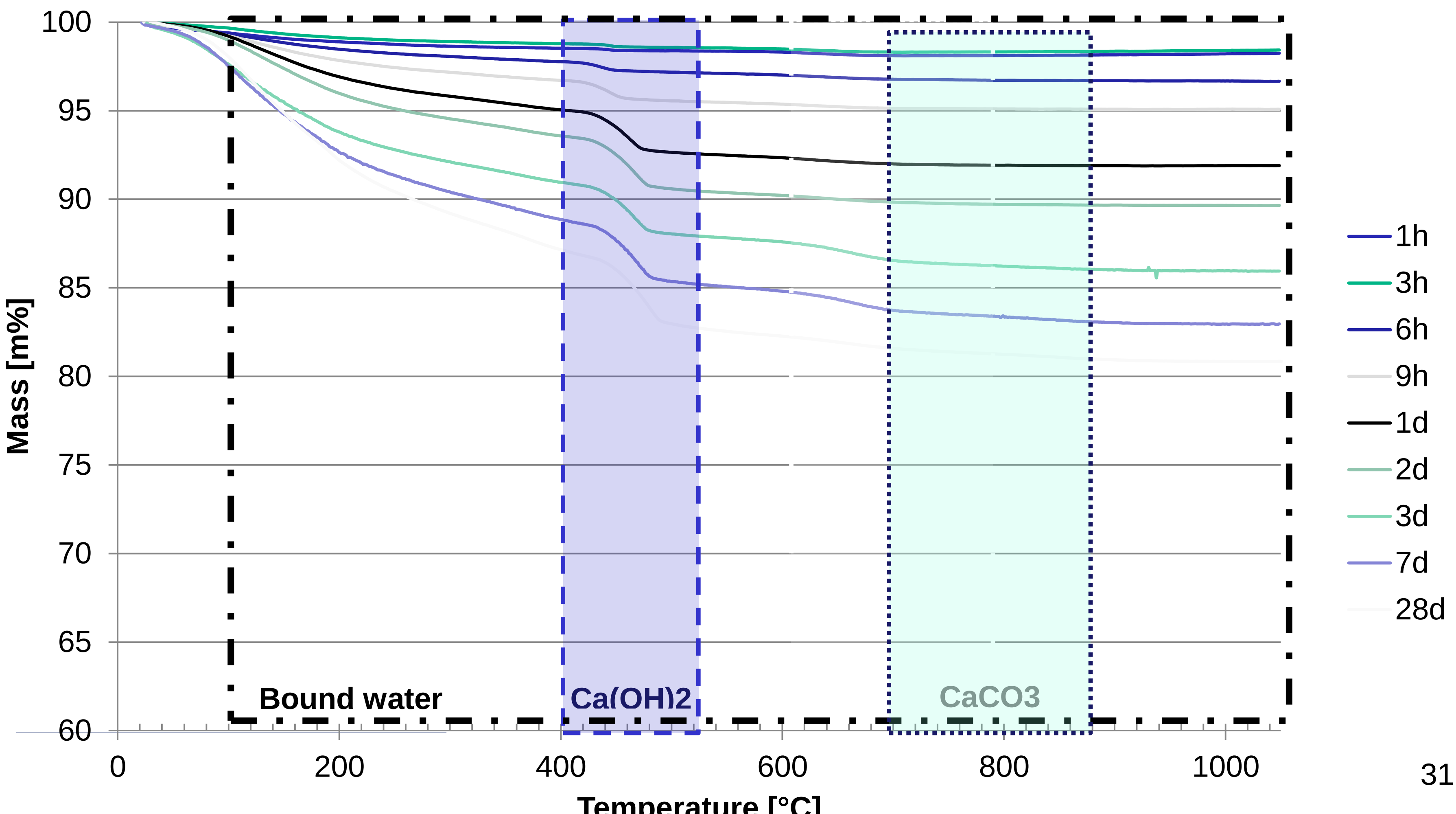
Measure of hydration:
- % bound water
- formation of $Ca(OH)_2$

TGA, DTA

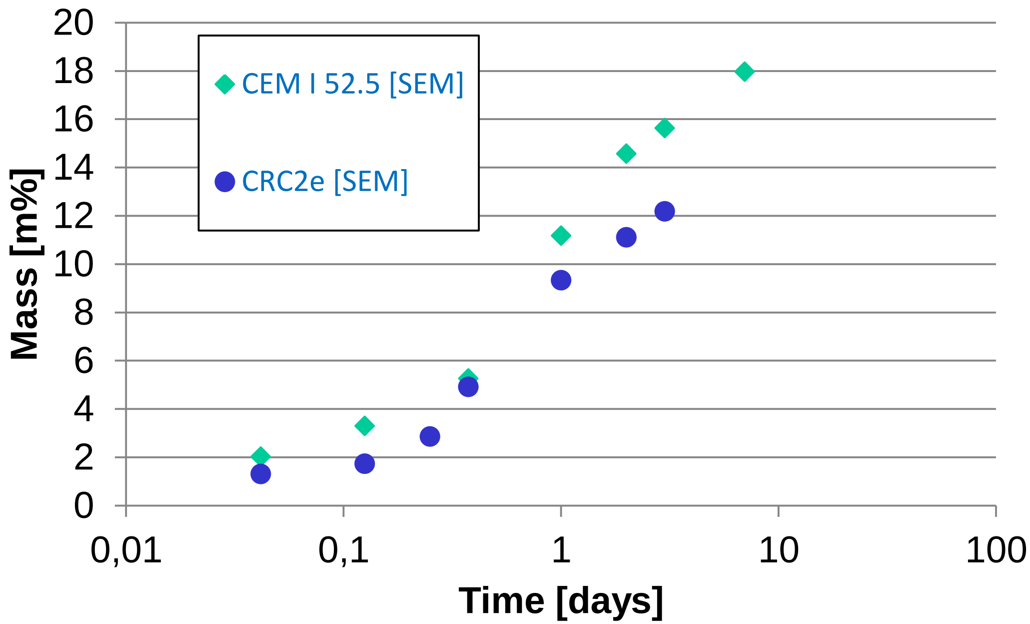
@ 10°C/min, N_2



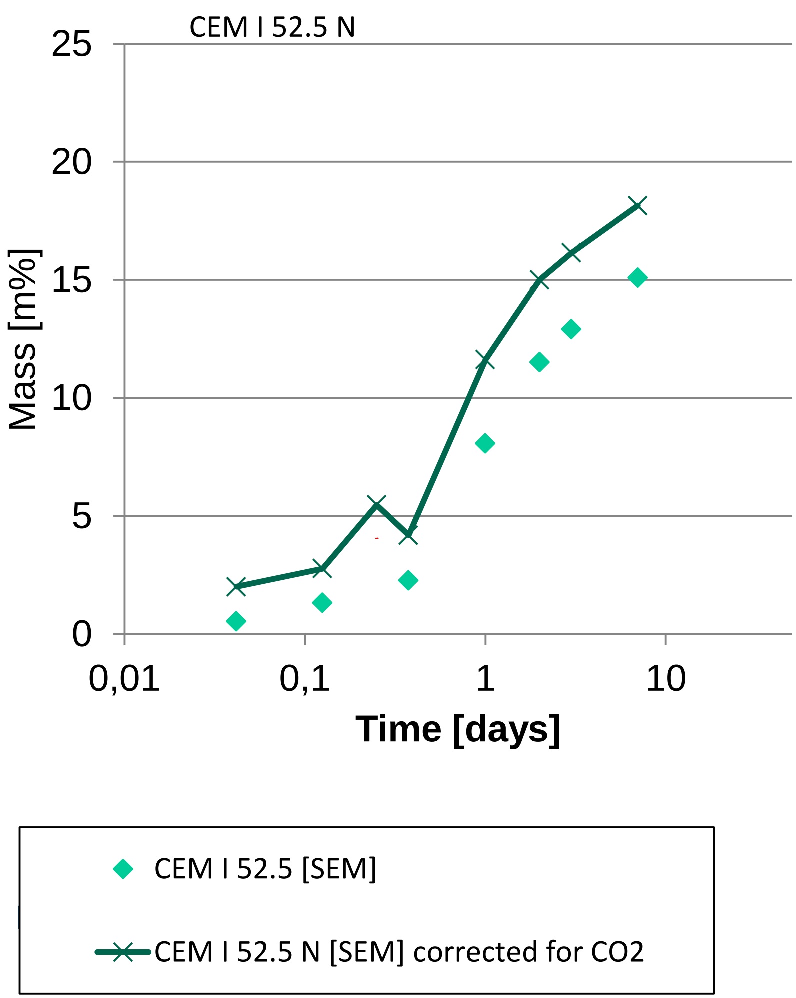
TGA, DTA

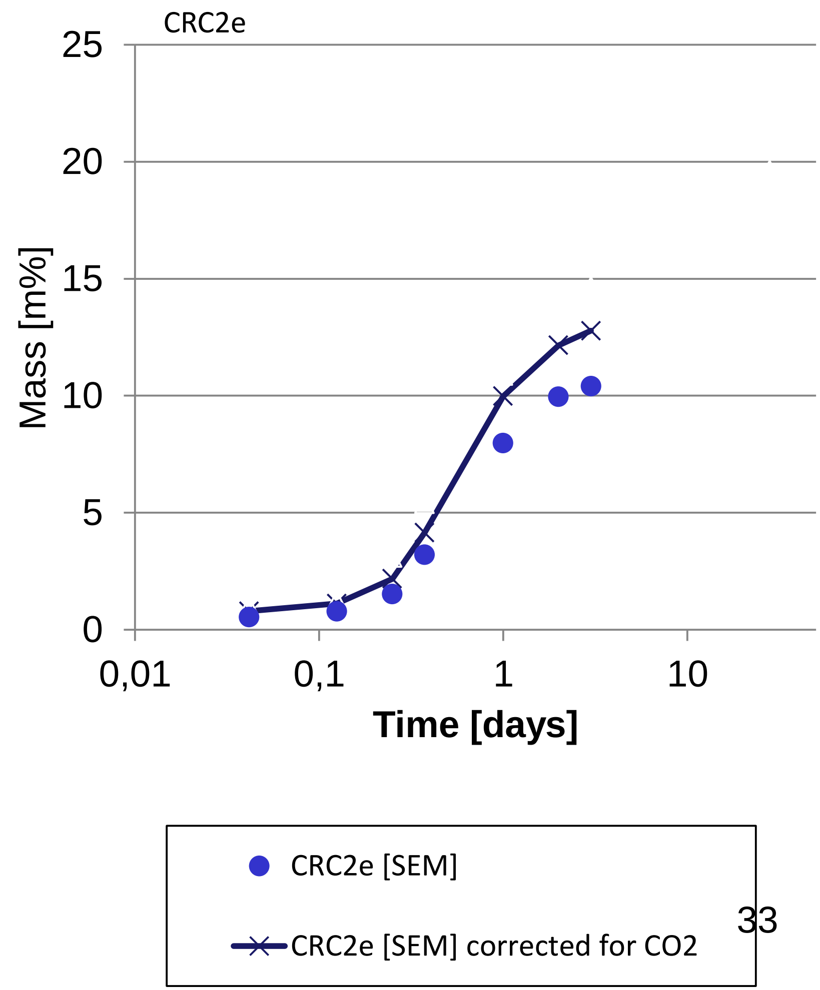

100
95
90
85
80
75
70
65
60
Mass [m%]
0
200
400
600
800
1000
Temperature [°C]
Bound water
Ca(OH)2
CaCO3
1h
3h
6h
9h
1d
2d
3d
7d
28d

TGA – Bound water content



TGA – Portlandite





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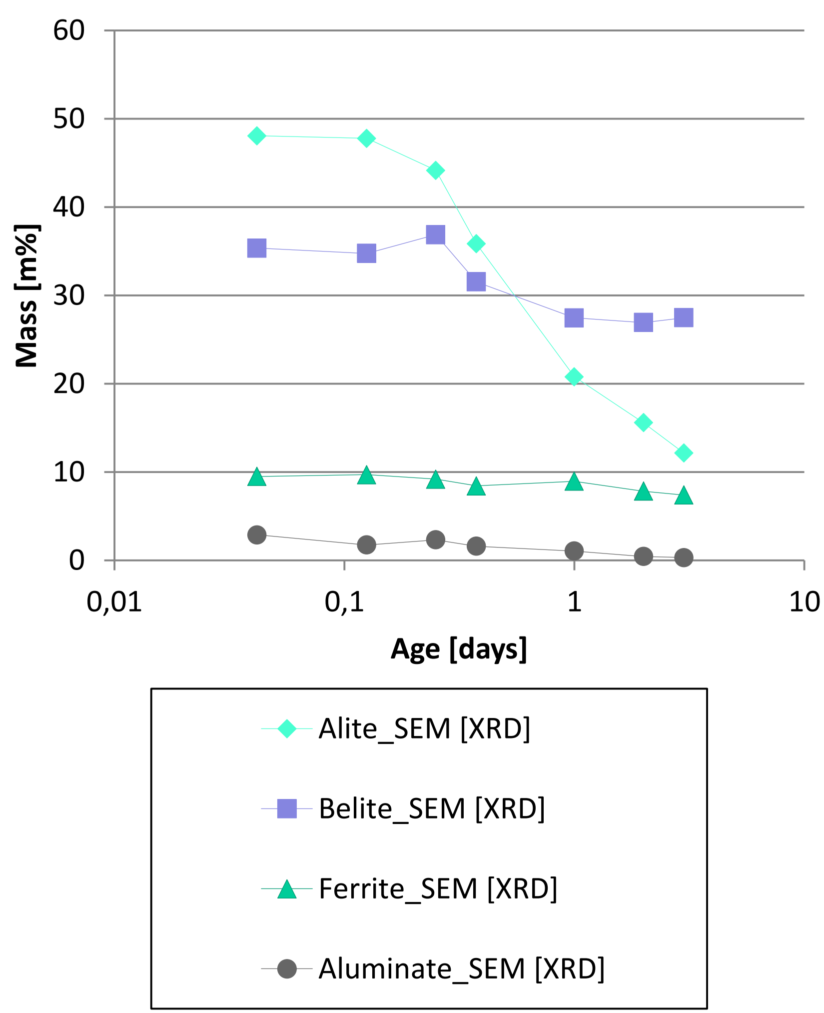
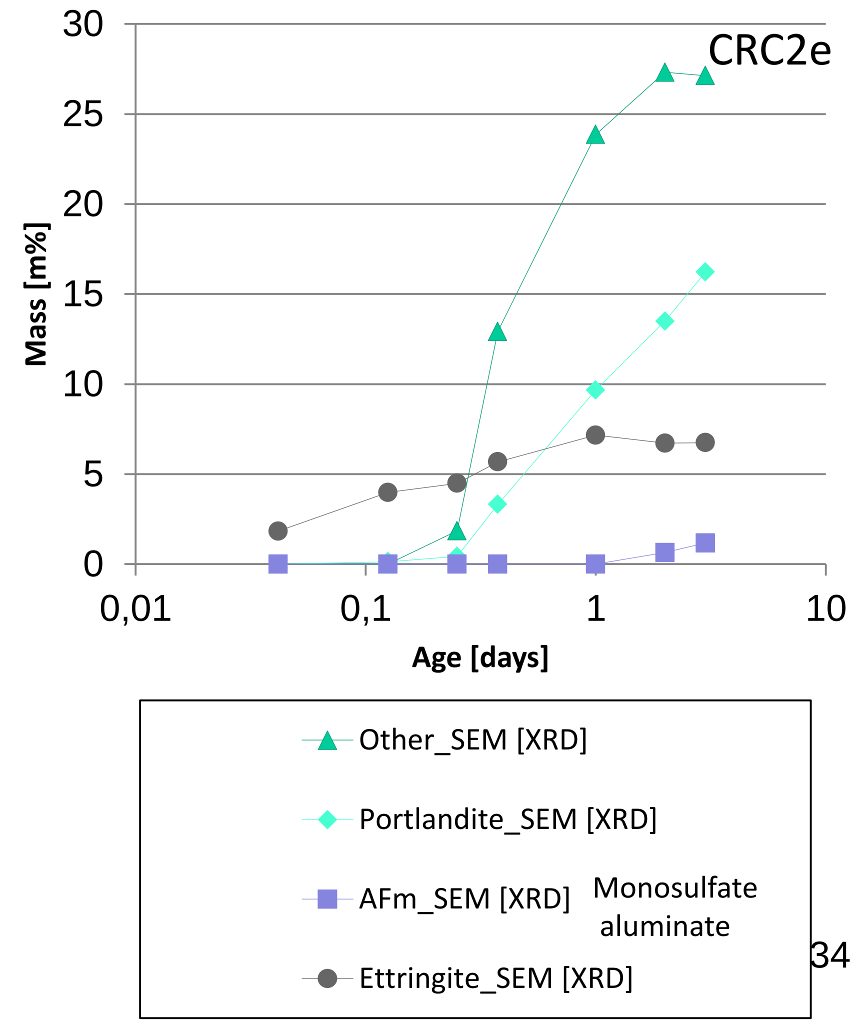
XRD, Rietveld

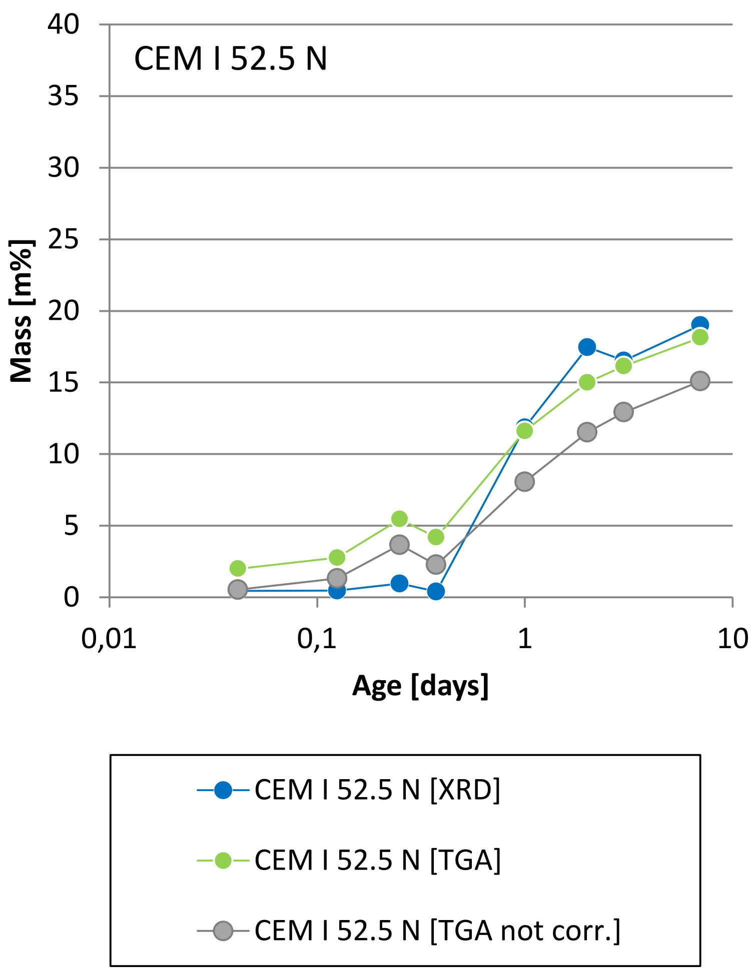
Hydration of clinker minerals …

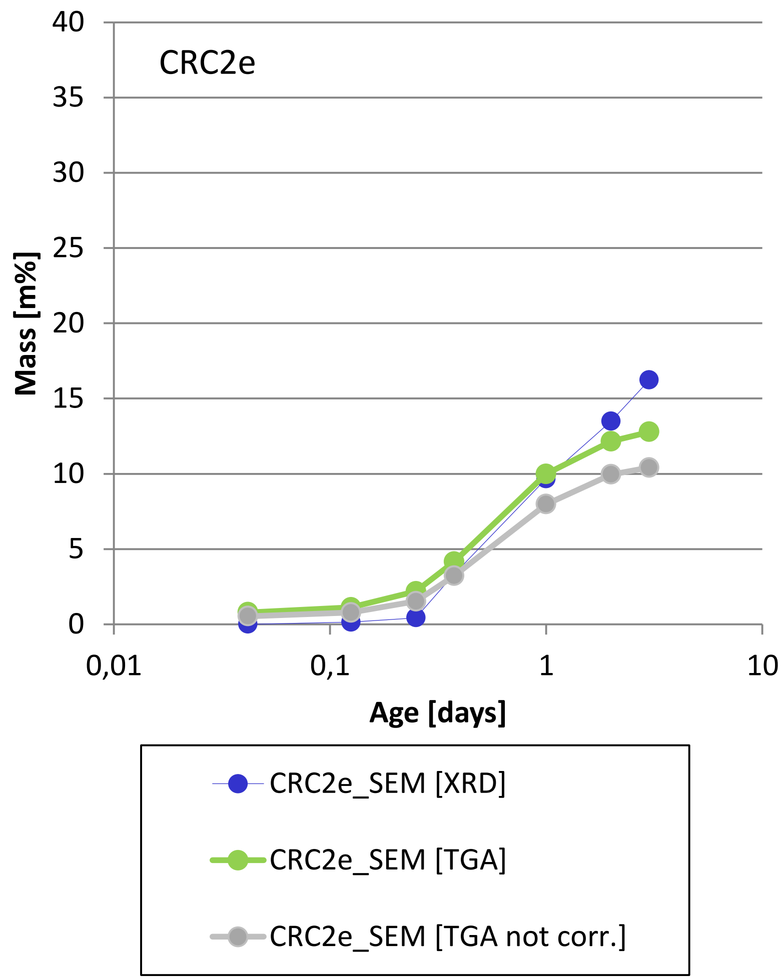


… Resulting in hydration products



Portlandite: TGA vs. XRD





Future:

design of the next CRC

Use of Waste fibrecement

Joris Schoon, Sagrex

Fibrecement: a non carbonate CaO source

less energy consumption to heat up
less CO_2 emission
= recycling: fibrecement is

Again: To make a good clincker:
composition should lie between certain limits

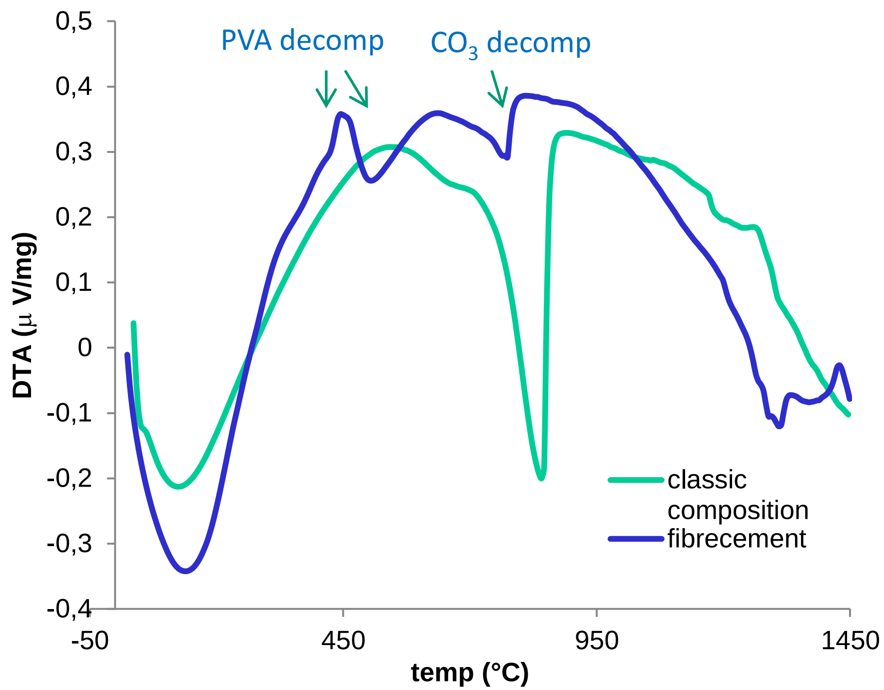
Most important:
- LSF: lime saturation factor Ca/ (Si, Al, Fe)
- SM: silica modus Si / Al, Fe
- AM: alumina modus Al / Fe

Ca : 60-65%

Use of Waste fibrecement

1. Thermogravimetry /Differential thermal analysis
   - Mass loss =>
     - amount CO_3 (600-800°C)
   - DTA => energy needed to heat till 1450°C
     - endotherm: decomp of CO3 (CaCO3 -> CaO +CO2 : 1782kJ/kg)
     - Endotherm: dehydration
   - TGA of fillers: determine decomposition temp. and products.

Use of Waste fibrecement



Emission of CO_2

» **1.6 billion tons** each year

~ 40% energy required for cement production (at > 1400 °C)

~ 60% calcination of limestone (to produce cement)

$$CaCO_3 \rightarrow CaO + CO_2$$

Energy to decompose fibres is small enough

Conclusions

Use of TGA , DTA, (HT- XRD) and calorimetry

Completely recyclable concrete

⇒ Characterise end products and study the reactions
- ⇒ During clinckering
- ⇒ And hydration
- ⇒ Identify end products and intermediates
- ⇒ Identify the difference in burnability
- ⇒ Follow reactions rate

⇒ Information for new design

Use of fibrecement

⇒ Could lead to Re-Use of fibrecement waste

⇒ Energy gain

⇒ Low CO2 emisions

⇒ industrial tests are the next step

"Clinckering Reactions during firing of recyclable concrete " R. Snellings J Am Cer Soc , 2012
"The hydration of cement regenerated from completely recyclable concrete" M. De Schepper, J Am Cer Soc, 2012
" Waste Fibrecement: An interesting alternative raw material for a sustainable Portland clinker production, J. Schoon , Construction and building materials, 36 (2012)